New vibrational assignments for the nu1 to nu17 vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between 720 cm-1 and 1050 cm-1

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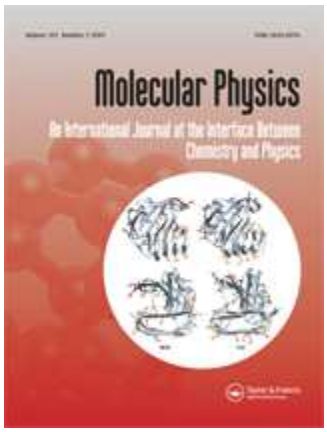

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New vibrational assignments for the ν_1 to ν_{17} vibrational modes of aziridine and first analysis of the high resolution infrared spectrum of aziridine between 720 cm^{-1} and 1050 cm^{-1}

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Abstract

Fourier transform spectra of aziridine (C_2H_4NH) were recorded at high resolution (0.002 or 0.003 cm^{-1}) in the 600-1750 and 1750-4000 cm^{-1} regions, using a Bruker IFS125HR (an upgraded version of the IFS120HR) spectrometer, located at the LISA facility in Creteil. In parallel, the harmonic force field of aziridine was evaluated analytically at the optimized geometry with second-order Møller–Plesset perturbation theory (MP2) together with the correlation-consistent polarized valence *triple* zeta basis sets cc-pVTZ. These ab initio predictions were used to perform consistent vibrational assignments for the ν_1 to ν_{17} fundamental bands of aziridine observed in the infrared spectra recorded during this study. Finally, a first detailed rotational assignment was performed for two B-type bands located at 772.3571 cm^{-1} (ν_{10}, CH_2 rock) and 997.1592 cm^{-1} (ν_8, NH bend) and for an A-type band located at 904.0429 cm^{-1} (ν_{17}, ring deform). We noticed that the ν_{10} band is weakly perturbed, presumably because the $\nu_{10} = 1$ rotational levels are coupled with those of the $\nu_{18} = 1$ dark band located around 817 cm^{-1} through B-type and C-type Coriolis resonances.

1. Introduction

Aziridine, *c*-C_2H_4NH, also called ethylenimine, is a three-membered heterocycle with an amine group. Its rotational spectrum has already been studied in details (see Refs. [1-3] and references herein). It is an oblate top (Ray's asymmetry parameter, $\kappa = +0.670$) which makes its centrifugal distortion analysis more difficult [3]. It is a molecule worth to be studied because of its potential astrophysical interest [1-3]. Aziridine is indeed a possible interstellar molecule candidate since many small nitrogen derivatives and epoxide [4] have already been observed in the Interstellar Medium. It could also be detected in the atmosphere of Titan [5]. Despite its interest, there is not much information on its infrared spectrum. As far as we know, the most recent papers are by Potts [6] Mitchell *et al.* [7] and by Gunasekaran and Uthra [8]. These authors proposed assignments for all fundamentals bands, based on low resolution Raman [6, 8] and infrared spectra [6-8] recorded for vapour phase and liquid phase for the main isotopic species of aziridine. In addition Mitchell et al. [7] used for its analysis infrared spectra recorded for imine-deuterated and ^{15}N isotopologues [7].

First let us mention that, according to [6, 7], no fundamental bands exist below 600 cm^{-1} and this is confirmed by the present study (See below). Therefore the analysis performed by Gunasekaran and Uthra [8] who assigned the first three fundamental vibrational bands of ethyleneimine at 526, 563, and 654 cm^{-1} respectively, is clearly incorrect and will not be considered further in the text. When comparing the experimental study performed by Mitchell *et al.* [7] and Potts [6] few of their vibrational assignments differ. On the otherhand some of their results are not compatible with the results of high-level ab initio calculations as shown below. For this reason, we have recorded at high resolution the infrared spectra of aziridine and reassigned all fundamental bands using all available experimental informations as well as results of ab initio calculations.

Finally, the rotational analysis of the ν_8, ν_{10} and ν_{17} bands was also undertaken and allowed us to determine both rotational and vibration rotation interaction constants which were compared to the ab initio predictions.

The present paper is organized as follows. Section 2 summarizes the experimental details. Section 3 describes the ab initio computational details. Using the ab initio predictions, the vibrational assignments for the ν_1 to ν_{17} bands were performed as described in Section 4. For the ν_8, ν_{10} and ν_{17} bands, a detailed rotational assignment could be performed (section 5).

2. Experimental details:

C_2H_4NH was prepared starting from 2-chloroethylamine hydrochloride (99 % stated purity, Sigma Aldrich) and sodium hydroxide (≥ 98 % stated purity, Sigma Aldrich). In a flask equipped with a reflux condenser, 2-Chloroethylamine hydrochloride (58 g, 0.5 mol), 90 ml of water and sodium hydroxide (60 g, 1.5 mol) were heated at 50°C for 2 hours. The solution was then distilled at reduced pressure until 70 mL of distillate had been collected. The cooled distillate was mixed with 35 g of sodium hydroxide, and the amine was distilled at atmospheric pressure through a one-foot column packed with glass helices. A 50 % sodium hydroxide solution was run in slowly at the top of the column during the distillation. The pot temperature did not exceed 70°C during the distillation. The aziridine was stored over a few pellets of sodium hydroxide. The yield ranges between 20 and 39 % in function of the efficiency of the stripping operation and the condensation of the low-boiling distillate but the yield of the Ref. [9] (73 %), has never been obtained.

The White-type multipass absorption cell, made of pyrex glass and equipped with CsBr windows, was connected to the Fourier transform spectrometer with a dedicated optical interface (six mirrors) inside the back sample compartment of the Bruker spectrometer. Its base length is 0.80 m, and, for the experiment described here, an optical path of 19.249 m was used. This value takes into account the distance between the surface of the field mirror and the windows of the cell (2 × 2.45 cm). The following procedure was used for measurements: first a background spectrum was collected while the cell was being continuously evacuated; next the infrared gas cell was treated with C_2H_4NH vapour several times, until no proton exchange with the surface could be detected and, for the final measurements sample pressures of 0.0341 (1) and 0.1188 (5) hPa were used. Sample pressure in the cell was measured using a calibrated MKS Baratron capacitance manometer (2 hPa full scale) which has a stated uncertainty of 0.12 % of full scale, according to the manufacturer. The absolute uncertainty given for the sample pressure is the sum of 0.12 % and 0.3 % for the variation of the pressure during the recording of the spectra. This gives an estimation of 0.42% on the pressure.

The infrared spectra of C_2H_4NH used in this study were recorded at high resolution in the 600-1750 and 1750-4000 cm^{-1} regions, using the Bruker IFS125HR Fourier transform spectrometer of the "Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA)" in Créteil, Paris. A KBr beamsplitter, Globar source (Silicon Carbide, SiC) and either a liquid nitrogen-cooled MCT photovoltaic detector or a liquid nitrogen-cooled InSb detector were employed for these experiments. The optical path of the spectrometer was continuously evacuated to below 0.05 hPa for the duration of all spectral measurements. Spectra were

recorded with an aperture diameter of 1.15mm, 40kHz scanner frequency, and a maximum optical path difference (d_{MOPD}) of 450 or 300 cm. According to the Bruker definition (Resolution = $0.9/d_{MOPD}$) this corresponds to a resolution of 0.002 cm^{-1} or 0.003 cm^{-1}. The spectra were recorded at a stabilized room temperature of 22°C. Both spectra were ratioed against the empty cell, single-channel background spectrum which was taken at a resolution of 0.512 cm^{-1}, in order to ensure the best possible signal-to-noise in the ratioed spectra. The spectra were the result of the co-addition of 570 interferograms. For the Fourier transform a Mertz-phase correction, 0.5 cm^{-1} phase resolution and boxcar apodization function were applied to the averaged interferograms. The spectra were calibrated using residual CO_2 and H_2O lines observed in the spectra, with their wavenumbers taken respectively from HITRAN08 [10] resulting in an accuracy of 0.0002 cm^{-1} (RMS) for well isolated lines.

3. *Ab initio* computational details

The harmonic force field of aziridine was evaluated analytically at the optimized geometry with second-order Møller–Plesset perturbation theory (MP2) [11] together with the correlation-consistent polarized valence *triple* zeta basis sets cc-pVTZ [12]. The coupled cluster method with single and double excitations [13] and a perturbative treatment of connected triples [14] [CCSD(T)] with the cc-pVTZ basis set was also used. The Kohn–Sham density functional theory [15] using Becke's three-parameter hybrid exchange functional [16] and the Lee–Yang–Parr correlation functional [17], together denoted as B3LYP was also used with the split-valence basis set 6-311G, as implemented in Gaussian03 (G03) [18], including appropriate polarization functions. It is indeed well established that multiplying the B3LYP harmonic frequencies by a scaling factor close to one (0.96-0.98) permits to obtain a rather accurate estimate of the fundamental frequencies [19].

In order to estimate the vibrational anharmonicity constants, the rotation-vibration interaction constants, and the Fermi interaction constants, the cubic (ϕ_{ijk}) and semi-diagonal quartic (ϕ_{ijkk}) normal coordinate force constants were determined at the same reference structure with the use of a finite difference procedure involving displacements along reduced normal coordinates (with step size $\Delta q = 0.03$) and the calculation of analytic Cartesian second derivatives at these displaced geometries [20, 21] using the MP2/cc-pVTZ method. The evaluation of anharmonic spectroscopic constants was based on second-order rovibrational perturbation theory [22].

The CCSD(T) computations were performed with the CFOUR [23] electronic structure program package, while the lower-level B3LYP and MP2 computations utilized the G03 program [18].

4 Vibrational assignments of the first seventeen (ν_1 to ν_{17}) fundamental bands of aziridine and rotational analysis of the ν_{10}, ν_{17} and ν_8 bands :

The aziridine structure [24, 25] is illustrated on Fig. 1. This non-planar C_s -type molecule possesses eighteen non-degenerate modes of vibration which are listed in Table 1. Of these, ten modes (ν_1 to ν_{10}) are of A' symmetry, while ν_{11} to ν_{18} are of A" symmetry. According to the selection rules for an electric dipole moment transition, infrared fundamental bands corresponding to an A" (respectively A') vibrational upper state are A-type bands (respectively hybrid-type bands, with both B- and C-type transitions). The A-type, B-type and C-type transitions correspond to (ΔK_a = even, ΔK_c = odd), (ΔK_a = odd, ΔK_c = odd) and (ΔK_a = odd, ΔK_c = even) rotational selection rules, respectively. Finally, transitions with (ΔK_a= even, ΔK_c = even) are forbidden in the infrared. In addition to these symmetry considerations, the observed line intensity pattern for each fundamental band is determined by the values of the components of the corresponding transition moment operators on the a-axis (for A' $\leftrightarrow$ A" vibrational transitions), or on the b- and c- inertia axes (for A' $\leftrightarrow$ A' or A" $\leftrightarrow$ A" vibrational transitions).

The ab initio calculations described in paragraph 3 were able to predict the band positions and intensities for aziridine fundamental bands. From these predictions, which are quoted in Table 1, it was easy to assign unambiguously the strong and well isolated fundamental bands in the observed experimental spectrum. Accordingly the positions measured in this work for the ν_2, ν_8, ν_9, ν_{11} and ν_{17} bands differ only marginally from those given previously in the literature [6, 7].

On the other hand, for medium intensity bands, such analysis is more difficult. In this case reliable and unambiguous vibrational assignments could be achieved only by performing detailed comparisons between theoretically-modeled and observed spectra.

To model the absorption for a given ν_i fundamental band (with i = 1 to 18), an approximate list of line positions and intensities was generated using the theoretical methods which are described in the next paragraph. The parameters necessary for these computations,

namely, the α_i^X (X = A, B and C) vibration rotation interaction constants, and the first order derivatives, $\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$ of the dipole moment operator (with β = a, b or c and q_i is the vibrational quantum coordinate associated to ν_i) collected in Table 2 are those deduced from the ab initio calculations. More explicitly, for the computation of the $v_i = 1$ upper state energy levels, we used the vibrational energy E_i which was adjusted slightly starting from its ab initio value (Table 1), and the α_i^X in order to get the variation of the upper rotational state constants relative to their ground state values [3]. To perform the intensity calculations the $\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$ dipole moment derivatives, were adjusted to within 10% of the values quoted in Table 2 in order to better reproduce the experimental spectra. Let us stress indeed that for hybrid bands, it is important to have a good value of the ratio $\left|\left(\frac{\partial \mu_b}{\partial q_i}\right)_0 \Big/ \left(\frac{\partial \mu_c}{\partial q_i}\right)_0\right|^2$.

Fig. 2 gives an overview of the aziridine spectrum in the 720 to 1050 cm^{-1} spectral range. As expected from symmetry consideration, the ν_{17} band at 904 cm^{-1} exhibits a narrow A-type Q structure. On the other hand, the ν_{10}, ν_9 and ν_8 bands, which should be hybrid, are in fact pure B- type bands, and this is what is indeed predicted by the ab initio calculations.

The vibrational assignments deduced in this way differ from the ones obtained from previous studies [6, 7] for several bands . For example, as can be seen on Fig. 3, the band located at 1266.67 cm^{-1} is the hybrid B- and C-type ν_5 band, with a strong C-type character, while in Refs. [6, 7] the Q structure near 1268 cm^{-1} was erroneously identified as the A-type ν_{14} band. On the other hand the ν_{14} band is presently located at 1237 cm^{-1}.

Fig. 4 shows a detailed view of the 3070-3090 cm^{-1} spectral region. It is clear that the ν_2 band at 3079.6 cm^{-1} is a C-type band which is significantly stronger than the A-type ν_{11} band at 3083.73 cm^{-1}. In Refs. [6, 7] both bands were assigned at 3079 cm^{-1}.

Finally we were unable to identify the ν_{18} band (CH_2 rock) which is expected to be extremely weak on the basis of the ab initio prediction. This band which is assumed to be observed near 817 cm^{-1} is in fact completely blended (see Fig. 2) under the stronger ν_{10} and ν_9 bands.

During this work it was also possible to perform a detailed rotational analysis of the ν_{10}, ν_{17} and ν_8 bands located at 773 cm^{-1}, 904 cm^{-1} and 998 cm^{-1}.

The first assignments were performed using calculated predictions both for line positions and relative intensities.

The upper and lower state energy levels were computed using, as it is usual in infrared, a Watson Hamiltonian written in the I^r representation with an A-type reduction. This choice of Hamiltonian reduction and axes representation need to be justified. Indeed, a recent detailed microwave study [3] performed for rotational transitions measured within the ground vibrational state of aziridine demonstrated that the combination of a S- reduction and a III^r representation lead to a better convergence of the ground state rotational Hamiltonian than when using the combination of a A-type reduction and I^r representation. However the improvements achieved in this way for the ground state energy levels concern Φ and L centrifugal distortion terms, which are Hamiltonian terms in J^6 and J^8, respectively. The present study concern the first vibrational states, for which the energy levels are affected by significant vibrational rotational resonances, as it will be demonstrated in the text. Since these perturbations could not be accounted for during the present study, the centrifugal distortion terms are clearly affected starting from terms in J^4 (Δ terms), and the preference for a (S, III^r) combination rather than (A,I^r) is not relevant for this infrared study.

Table 3 gives the (A,I^r) rotational Hamiltonian used during the present study. The rotational and centrifugal distortion constants quoted in the last column of Table 2 of Ref. [3] and gathered in Table 4 of this work were used for the computation of the ground state levels during all this study. For the upper vibrational states, the preliminary values of the rotational constants were computed from the α_i^X vibration rotation interaction constants predicted by the ab initio calculations, and using the approximation:

$$X_i = X_0 - \alpha_i^X \quad \text{(with X = A, B and C)} \qquad \text{Eq. (1)}$$

In this expression, the X_0 are the ground state rotational constants of Ref. [3], while the centrifugal distortion constants were maintained at their ground state values during the first calculations.

The line intensities calculations were performed using the method described elsewhere [26], and the first order derivatives, of the dipole moment operator deduced from ab initio calculations.

Using these predictions, some low and medium J and K_a transitions in the ν_{10}, ν_8 and ν_{17} bands were assigned. Then, using the ground state parameters of Ref. [3], the lower state

energy levels were calculated and added to the newly observed line positions to get a list of experimental upper state energy levels. These upper state levels were inserted in a least squares fit to get an improved set of upper states parameters allowing better predictions and hence more assignments to be made. Gradually the vibrational energies and the rotational and centrifugal distortion constants were refined for the 10^1, 8^1 and 17^1 vibrational states during the assignment process. This iterative process was carried out until the ν_{10}, ν_8 and ν_{17} bands were completely assigned.

No noticeable perturbations were noticed during the analysis of the ν_8 and ν_{17} bands. However, at a given level, it appeared that transitions of the ν_{10} band involving $K'_c \approx 20$ and $K'_c \approx 8$ rotational quantum numbers in the upper levels are perturbed. It is presumed that the 18^1 dark state, located near 817 cm^{-1} is involved in the perturbations observed for the ν_{10} band, since the ab initio calculations predict rather significant C-type Coriolis resonances coupling the $10^1 \Leftrightarrow 18^1$ energy levels (with $\varsigma^{B}_{10,18} = -0.025$ and $\varsigma^{C}_{10,18} = -0.490$ for the B- and C- type Coriolis parameters, respectively).

The results of the final assignments, in term of ranges of the upper state rotational quantum numbers, are given in the upper part of Table 5. Examples of assignments for the ν_{10}, ν_{17}, and ν_8 bands are given in Figs. 5, 6 and 7, respectively.

The same procedure was tentatively applied for the B-type ν_9 band at 855.94 cm^{-1}. However at a given level, it appeared that this band is extremely perturbed: we think that strong B- and C-type resonances are coupling the 9^1 upper state energy levels with those of the 18^1 dark state. This is indeed expected from the results of the ab initio calculations which predict $\varsigma^{B}_{9,18} = -0.113$ and $\varsigma^{C}_{9,18} = -0.800$ for the B- and C- type Coriolis parameters, respectively. Unfortunately it was not possible to go in more detail in the analysis of the resonance since no experimental data exist, up to now, for the $\nu_{18} = 1$ dark state.

Table 4 lists the Hamiltonian constants (vibrational energies, rotational and centrifugal distortion constants) resulting from the final fits of the 10^1, 8^1 and 17^1 upper state energy levels, together with their associated statistical uncertainties. For this calculation, the set of 10^1 energy levels was restricted to the set of unperturbed energy levels. As usual the parameters derived for the higher order centrifugal distortion constants are effective with poor physical meaning. This is mainly true for the 10^1 vibrational state, for which clear resonances

are observed. This is also the case for the 17^1 state. Although no noticeable perturbation could be observed during the assignment of the ν_{17} band, the ab initio calculations predict that B and C-type Coriolis resonances are coupling together the $17^1 \Leftrightarrow 8^1$ energy levels (with $\varsigma^{B}_{17,8} = -0.1131$ and $\varsigma^{C}_{17,18} = -0.7997$ for the B- and C- type Coriolis parameters, respectively).

The results of the energy levels calculations proved to be rather satisfactory, as can be seen from the standard deviation and statistical analysis given in the lower part of Table 5.

It is interesting to compare the observed and calculated spectra.

Figure 2 shows the overview of the observed and calculated spectra in the 720 cm^{-1} to 1050cm^{-1} region. The perturbed ν_9 band, whose analysis is in progress, is not plotted on the calculated spectrum.

Figures 5 and 6 show portions of the Q branch of the ν_{10} and ν_{17} bands, respectively. Fig. 7 gives a portion of the R branch of the ν_8 band. In each case the agreement between the observed and calculated spectra is excellent.

Finally the values of the experimental α_i^X vibration rotation interaction constants are compared in Table 6 to these ab initio values, showing a reasonable agreement for the three bands under study.

8. Conclusion

A new vibrational assignment was performed for the fundamental bands of aziridine, based on ab initio calculations and on Fourier transform spectra recorded at high resolution. In addition the first analysis of the ν_{10}, ν_8 and ν_{17} fundamental bands of aziridine was performed. No noticeable perturbations were observed during the analyses of ν_8 and ν_{17} bands, while the ν_{10} band appears to be weakly perturbed. The energy levels resulting from the analyses were used to derive accurate vibrational energies, and rotational and centrifugal distortion constants for the 8^1, 10^1 and 17^1 vibrational states.

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Captions of the figures:

Fig. 1. Structure of the aziridine molecule [24, 25].
The a, b and c are the inertial axes and (bc) is the symmetry plane for this non planar C_s -type molecule. The I^r representation (x = b, y = c and z = a) was adopted for all calculations.

Fig. 2. Overview of the aziridine spectrum in the 720-1050 cm^{-1} region ($\nu_{10,}$ ν_9, ν_{17} and ν_8 bands).
The narrow Q branch structure at 904 cm^{-1} indicates an A-type structure for the ν_{17} band. The ν_{10}, ν_9 and ν_8 hybrid bands which do not exhibit any sharp Q structure are mainly B-type bands.
Lower trace: observed spectrum recorded with a resolution of 0.002 cm^{-1} and an optical path length of 19.249 m, at a C_2H_4NH pressure of 0.0341 hPa and a stabilized room temperature of 295.2 K. Upper trace: the synthetic spectrum, calculated for the ν_{10} , ν_{17} and ν_8 bands is shifted vertically for a clear comparison. The ν_9 perturbed band is not considered in the present analysis (see text).

Fig. 3. Overview of the ν_5 band of aziridine in the 1267 cm^{-1} spectral region.
Medium trace: observed spectrum (see the caption of Fig. 2). Upper trace: low resolution model for the ν_5 hybrid (both B- and C-type) band (see text). The model assuming an A-type character for this band is clearly incorrect.

Fig.4. Overview of aziridine infrared spectrum in the 3080 cm^{-1} spectral region.
Lower trace: observed spectrum recorded with a resolution of 0.003 cm^{-1} and an optical path length of 19.249 m, at a C_2H_4NH pressure of 0.1188 hPa and a stabilized room temperature of 295.2 K. Upper trace: calculated ν_2 C-type band and ν_{11} A-type band at 3079.6 and 3083.73 cm^{-1}, respectively.

Fig. 5. Portion of the Q branch of the ν_{10} band of aziridine in the 763 cm^{-1} spectral region.
The $^{P,R}Q_{Kc}$ structure for K''_c = 13 (solid triangles) is presented together with some additional assignments. The d letters stand for degenerate transitions with K_a = J-K_c and K_a = J-K_c+1). Excellent agreement is obtained between the observed (lower) and the calculated (upper) spectrum.

Fig. 6. Portion of the Q branch of the ν_{17} band of aziridine in the 903.5 cm^{-1} spectral region. Together with additional assignments, series of $^{Q}Q_{K_a}(J)$ are presented for the $K_a = J$ and $K_a = J-1$ series by solid and open triangles, respectively. For both series, the d letter stands for $K_c = J-K_a$ and $J-K_a+1$ values.
Excellent agreement is obtained between the observed (lower) and the calculated (upper) spectrum.

Fig. 7. Portion of the R branch of the ν_8 band of aziridine in the 1013 cm^{-1} spectral region. For this oblate molecule, the [J', K'_a = d, K'_c] ← [J" = J'-1, K''_a = d, K''_c] series of R transitions are grouped in stacks corresponding to equal values of s'= (2J'- K'_c). Examples of such stacks are given for s = 18, 19 and 20, and the assignments are for the upper level J' values (d stands for degenerate transitions with $K_a = J-K_c$ and $K_a = J-K_c+1$).
Excellent agreement is obtained between the observed (lower) and the calculated (upper) spectrum.

Captions of the tables:

Table 1:

Vibrational modes for aziridine.

Caption :

a: Harmonic frequencies calculated at the B3LYP/6-311+G(3df,2pd) level of theory, see text.
b: CCSD(T)/cc-pVTZ for the harmonic part and MP2/cc-pVTZ for the anharmonic correction.
c: Band intensity in km/mol, calculated with the double harmonic approximation at the CCSD(T)/cc-pVTZ level of theory.
d: Ref. [6].
e: Ref. [7].
f: High resolution study (this work).
g: For these bands, only the band center could be determined (this work).
h: This band is a dark band.

Table 2:

Vibration rotation interaction constants α_i^X (X = A, B and C). Components on the (β = a, b or c) molecular axes of the first order derivatives, $\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$ of the dipole moment operator.

Caption:

i (i = 1, 18) are the eighteen molecular vibrational modes (see Table 1). α_i^X and $\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$ are expressed in MHz and in atomics units (au/($u^{½}$. Å)), respectively. One has, 1 au = 2.54174691 Debye = $8.47835281.10^{-30}$ C.m, 1u = $1.660538782(83)\times10^{-27}$ kg, and 1Å = 10^{-10} m.

Table 3:

Watson's type Hamiltonian (I^r representation)

Table 4:

Vibrational energies, and rotational and centrifugal distortion constants for the ground state and the 8^1, 10^1 and 17^1 vibrational states of aziridine.

Caption :

The vibrational energies are in cm^{-1}, and all other parameters are in MHz, KHz, Hz or mHz. The quoted errors are one standard deviation.

(a) Ref. [3];

(b) fixed at the ground state value [3].

Table 5:

Results of the analyses of the ν_{10}, ν_{17} and ν_8 bands.

Statistical analysis of the energy levels calculation.

Table 6:

Experimental and ab initio values for the α_i^X (X = A, B or C) vibration rotation interaction constants (in MHz)

Table 1

Band centers of aziridine (in cm^{-1})

			Ab initio			Experimental		
		Sym.	B3LYP[a]	CCSD(T)/ cc-pVTZ [b]	Intensity[c]	d	e	This work
1	NH stretch	A'	3514.1	3527.4	0.67	3338	3346	3337.4 [f]
2	CH_2 a-stretch	A'	3194.2	3231.2	25.48	3079	3079	3079.6 [f]
3	CH_2 s-stretch	A'	3108.1	3157.2	13.53	3015	3015	3002.8 [f]
4	CH_2 scissor	A'	1526.7	1543.9	0.83	1481	1483	1482.9 [f]
5	ring stretch	A'	1294.4	1315.0	7.53	1210	1210	1266.67 [f]
6	CH_2 twist	A'	1239.1	1253.3	13.96	1131	1096	1210.2 [f]
7	CH_2 wagging	A'	1116.6	1125.9	6.63	1089.5	1090	1089.4 [f]
8	NH bending	A'	1006.0	1018.6	8.58	997.5	998	997.1592 [g]
9	ring deformation	A'	870.3	889.8	50.20	856	856	855.94 [f]
10	CH_2 rocking	A'	778.7	784.3	19.64	772.5	772	772.3571 [g]
11	CH_2 a-stretch	A"	3180.9	3217.4	0.54	3079	3079	3083.73 [f]
12	CH_2 s-stretch	A"	3103.1	3148.8	25.89	3015	3003	3015.6 [f]
13	CH_2 scissor	A"	1499.8	1511.9	0.04	1462.5	1462	1462.2 [f]
14	CH_2 twist	A"	1237.4	1276.8	8.37	1268	1268	1237 [f]
15	NH bending	A"	1154.8	1165.0	2.08	1237	1237	1130.4 [f]
16	CH_2 wagging	A"	1124.7	1123.4	2.49	1095	1131	1096.2 [f]
17	ring deformation	A"	919.4	920.5	12.51	903.5	904	904.0429 [g]
18	CH_2 rocking	A"	857.3	865.8	0.00	817	(820)	Dark [h]

Table 2

Vibration rotation interaction constants α_i^X (X = A, B or C). , Components on the (β = a, b or c) molecular axes of the first order derivatives, $\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$ of the dipole moment operator.

		α_i^X			$\left(\frac{\partial \mu_\beta}{\partial q_i}\right)_0$		
	Position (cm^{-1})	X = A	X = B	X = C	β = a	β = b	β = c
i = 1	3337.4	82.95	25.34	17.50	0	-0.0261	0.0032
2	3079.6	12.41	37.00	12.98	0	-0.0129	0.1612
3	3002.8	23.81	41.91	8.74	0	-0.1142	-0.0287
4	1482.9	-7.16	45.88	-28.71	0	-0.0210	0.0201
5	1266.67	-25.70	-134.91	-106.15	0	0.0777	0.0412
6	1210.2	37.62	195.78	444.15	0	-0.1190	-0.0124
7	1089.4	17.97	-4.13	107.82	0	0.0824	-0.0035
8	997.1592	58.06	13.57	94.92	0	-0.0938	-0.0035
9	855.94	18.44	47.29	-554.17	0	-0.2266	-0.0116
10	772.3571	-13.26	54.88	166.43	0	-0.1419	0.0052
11	3083.73	16.69	30.24	12.33	0.0235	0	0
12	3015.6	23.63	39.41	7.87	0.1630	0	0
13	1462.2	-22.80	25.98	-41.72	-0.0064	0	0
14	1237	-19.73	-62.60	-297.39	-0.0926	0	0
15	1130.4	-50.98	69.80	-127.77	-0.0462	0	0
16	1096.2	48.33	17.46	37.30	0.0506	0	0
17	904.0429	98.38	-15.44	-177.68	-0.1133	0	0
18	dark	214.10	10.17	756.74	-0.0014	0	0

Table 3

Watson A-type rotational Hamiltonian written in the I^r representation.

$$H_W = E_v + \left[A_v - 1/2\left(B_v + C_v\right)\right] J_z^2 + 1/2\left(B_v + C_v\right) J^2 + 1/2\left(B_v - C_v\right) J_{xy}^2$$
$$- \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 \mathbf{J}^2 - \Delta_J^v \left(\mathbf{J}^2\right)^2 - \delta_K^v \left\{J_z^2, J_{xy}^2\right\} - 2\delta_J^v J_{xy}^2 \mathbf{J}^2$$
$$+ H_K^v J_z^6 + H_{KJ}^v J_z^4 \mathbf{J}^2 + H_{JK}^v J_z^2 \left(\mathbf{J}^2\right)^2 + H_J^v \left(\mathbf{J}^2\right)^3$$
$$+ h_K^v \left\{J_z^4, J_{xy}^2\right\} + h_{KJ}^v \left\{J_z^2, J_{xy}^2\right\} J^2 + 2h_J^v J_{xy}^2 \left(J^2\right)^2$$
$$+ L_K^v J_z^8 + L_{KKJ}^v J_z^6 J^2 + L_{KJ}^v J_z^4 (J^2)^2 + L_{JJK}^v (J^2)^2 + L_J^v (J^2)^4$$
$$+ l_K^v \left\{J_z^6, J_{xy}^2\right\} + l_{KJ}^v \left\{J_z^4, J_{xy}^2\right\} J^2 + l_{JK}^v \left\{J_z^2, J_{xy}^2\right\} J^2)^2 + 2l_J^v J_{xy}^2 (J^2)^3$$
$$+ P_K^v J_z^{10} + P_{KKKJ}^v J_z^8 J^2 + P_{KKJ}^v J_z^6 J^4 + \ldots$$

with: $\{A,B\} = AB + BA$ and $J_{xy}^2 = J_x^2 - J_y^2$

Table 4

Vibrational energies, and rotational and centrifugal distortion constants for the ground state and the 10^1, 17^1 and 8^1 vibrational states of aziridine.

	Ground [(a)]	10^1	17^1	8^1
E_V		772.35710 (95)	904.042857 (76)	997.159192 (21)
A/MHz	22736.172428	22745.759(319)	22634.3242(431)	22666.6856(119)
B/MHz	21192.486318	21133.107(232)	21202.3339(324)	21177.41211(916)
C/MHz	13383.159073	13187.563(204)	13488.6240(149)	13275.75195(454)
Δ_J /KHz	18.9965530	16.336(269)	23.6076(354)	16.98074(955)
Δ_{JK} /KHz	9.25169	26.198(874)	-3.020(129)	12.2790(305)
Δ_K /KHz	20.05041	6.046(782)	27.601(145)	18.4084(406)
δ_J /KHz	5.880024	7.1253(739)	3.8068(178)	6.76170(429)
δ_K /KHz	12.70180	b	16.8013(172)	10.32504(773)
H_J /Hz	-0.007240	-0.501(103)	0.2294(183)	-0.07287(259)
H_{JK} /Hz	0.49776	b	-1.2833(929)	b
H_{KJ} /Hz	-1.91427	-7.49(120)	1.803(164)	b
H_K /Hz	1.51860	7.31(108)	-0.377(159)	1.5646(241)
h_J /Hz	-0.003784	b	-0.11888(921)	b
h_{JK} /Hz	0.21084	b	b	b
h_K/Hz	-0.28571	b	b	b
L_{JJK}/mHz	-0.002039	b	b	b
L_{JK}/mHz	0.00619	b	b	b
L_{KKJ}/mHz	-0.00837	b	b	b
L_K/mHz	0.00323	b	b	b
l_J/mHz	-0.0000531	b	b	b
l_{JK}/mHz	-0.001007	b	b	b
l_{KJ}/mHz	0.004547	b	b	b
l_K/mHz	-0.006888	b	b	b

Table 5

Some details about the observed energy levels

Band	ν_{10}	ν_{17}	ν_{8}
Number of lines	2497	2875	1959
Vibrational state :	18^1	7^1	16^1
J_{Max} =	47	47	45
K_a	$K_a \leq 40$	$K_a \leq 30$	$K_a \leq 34$
Number of levels	753	1290	811

Statistical analysis of the energy levels calculation:

Vibrational states	$\mathbf{10^1}$	$\mathbf{17^1}$	$\mathbf{8^1}$
Number of levels:	753	1290	811
Number of levels considered in the least squares fit:	731	1290	811
$0 \leq \delta < 0.5x10^{-3}\ cm^{-1}$	52.94%	90.39%	96.42%
$0.5x10^{-3} \leq \delta < 1x10^{-3}\ cm^{-1}$	18.06%	6.20%	3.08%
$1x10^{-3} \leq \delta < 2x10^{-3} cm^{-1}$	17.51%	2.95%	0.49%
Standard deviation (10^{-3} cm^{-1}):	41.47	4.15	1.29

$\delta = |E_{obs} - E_{calc}|$ in 10^{-3} cm^{-1}

Table 6

Experimental and ab initio values for the α_i^X (X = A, B or C) vibration rotation interaction constants (in MHz)

	10^1		17^1		8^1	
α_i^X	Exp	Ab Initio	Exp	Ab Initio	Exp	Ab Initio
α_i^A	-9.59	-13.26	101.85	98.38	69.49	58.06
α_i^B	59.38	54.88	-9.85	-15.44	15.07	13.57
α_i^C	195.60	166.43	-105.46	-177.68	107.41	94.92

Fig. 1

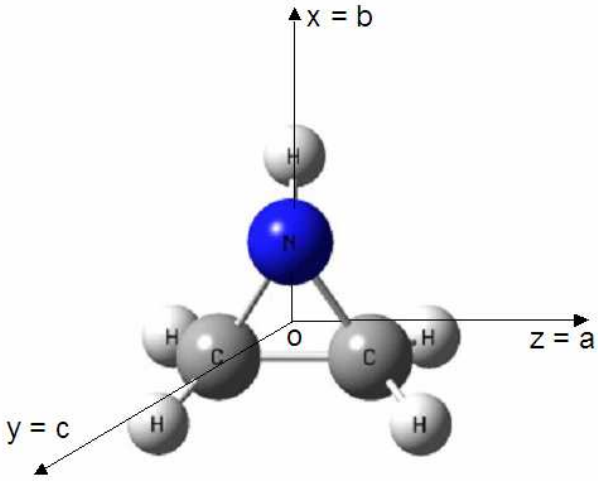


Fig.2

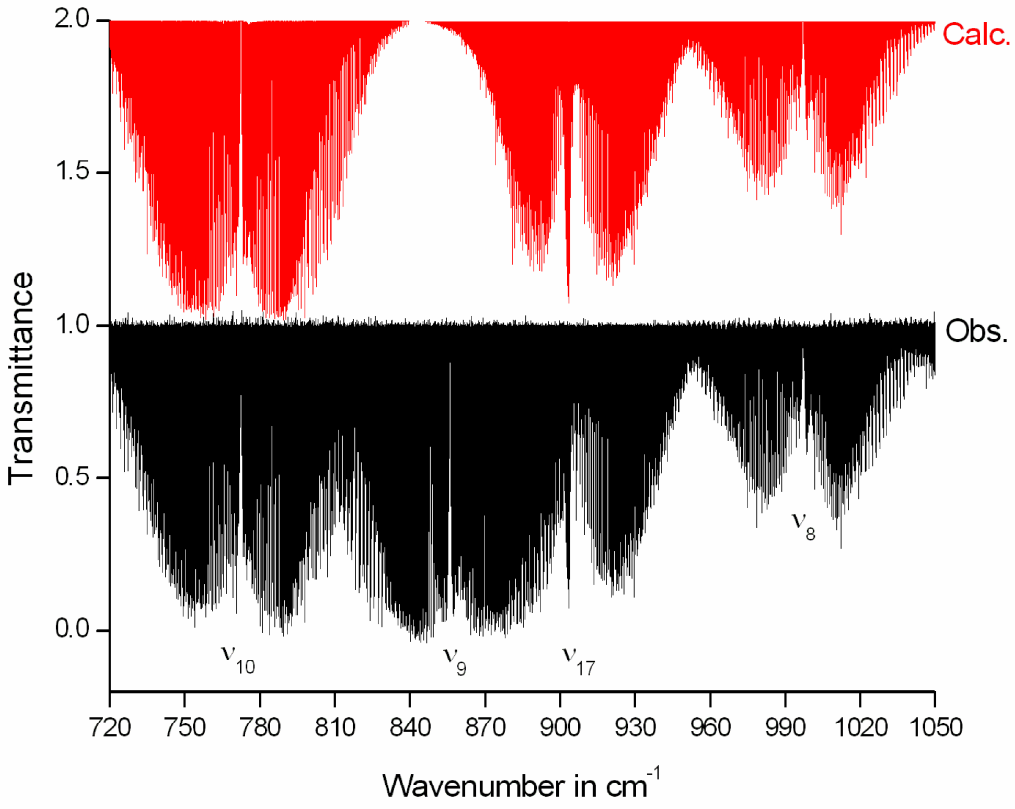


Fig.3

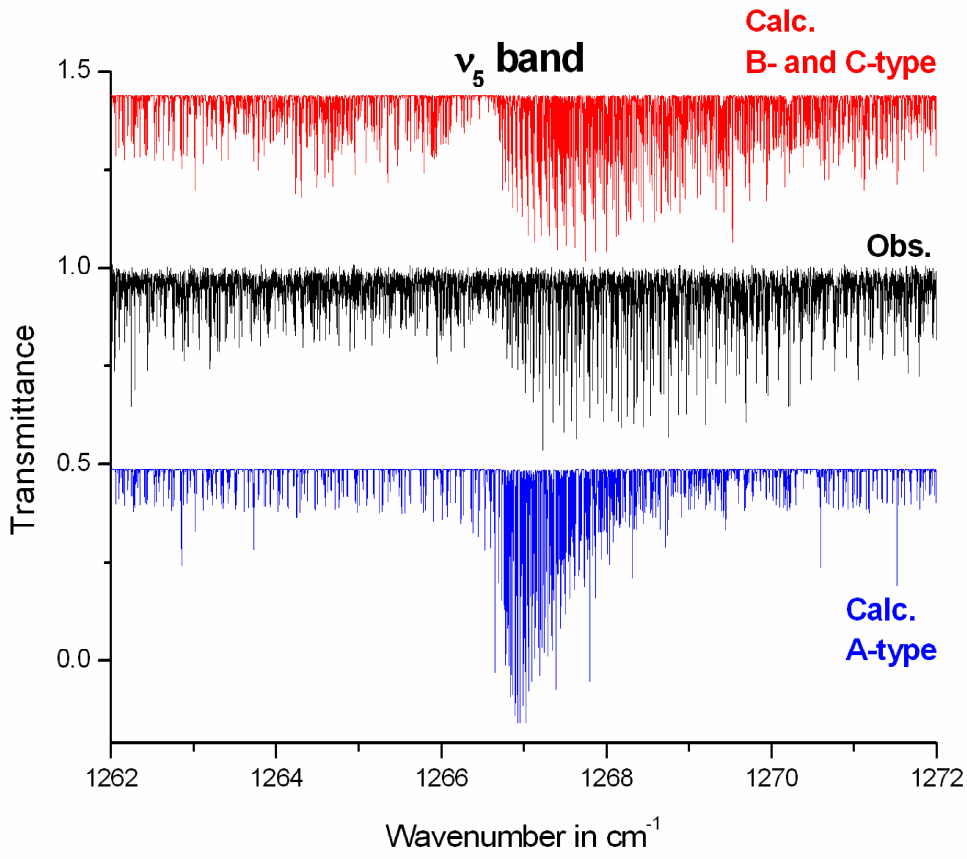


Fig.4

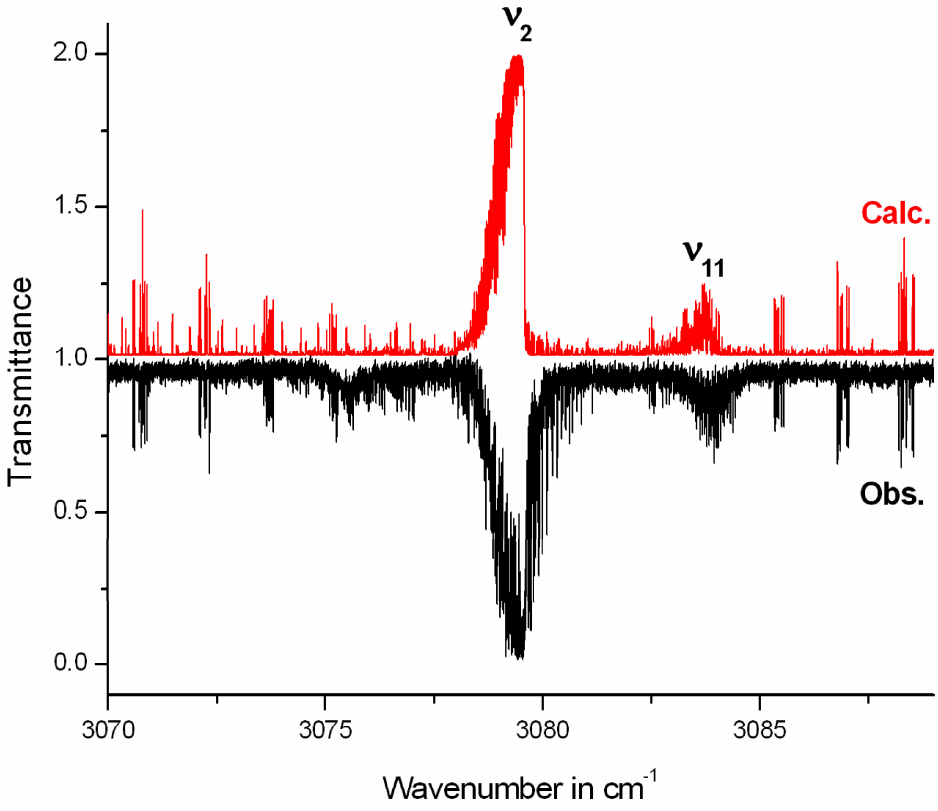
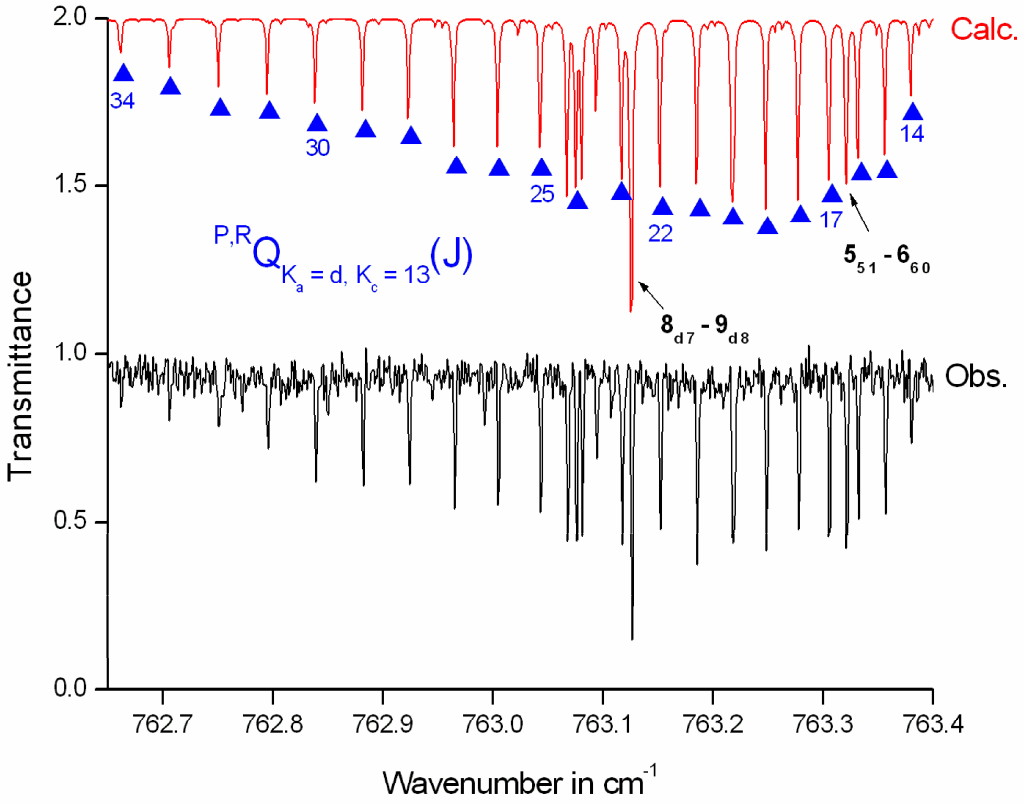


Fig.5



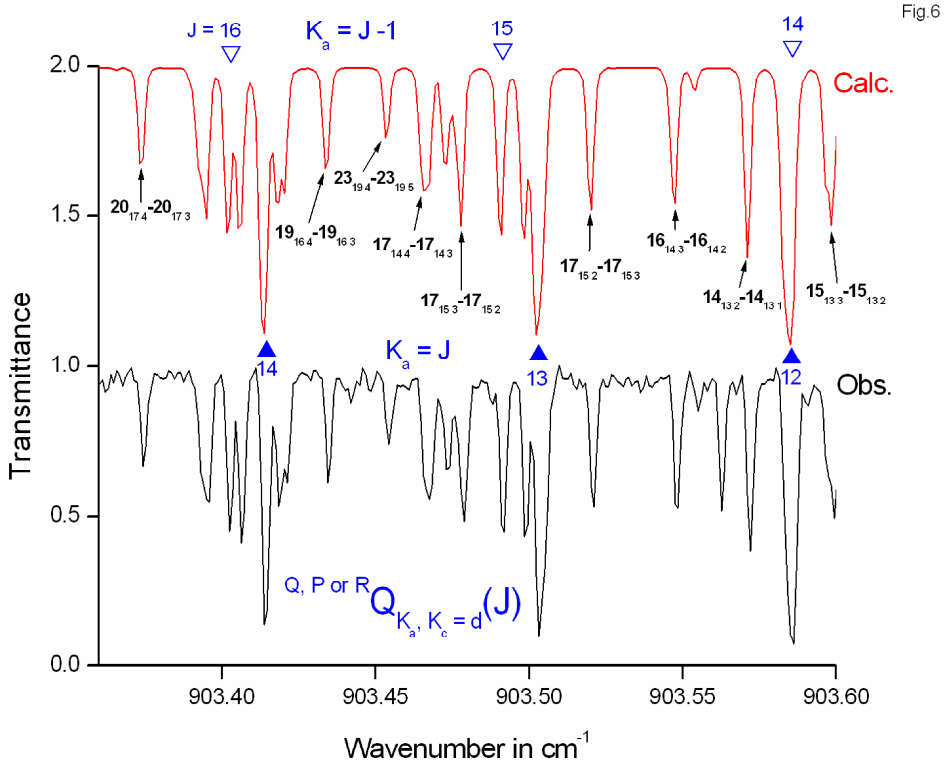


Fig.6

Fig.7